



OFICINA ESPAÑOLA  
DE PATENTES Y MARCAS  
ESPAÑA

⑪ ES 2 092 429

⑫ N.º solicitud: 9301712

⑬ Fecha de presentación de la solicitud: 29.07.93

⑭ Fecha de prioridad:

## INFORME SOBRE EL ESTADO DE LA TECNICA

⑮ Int. Cl.<sup>6</sup>: B01D 53/60, 53/86, B01J 21/00, C10G 11/04

### DOCUMENTOS RELEVANTES

Categoría	Documentos citados	Reivindicaciones afectadas
Y	US 4492678 A (ATLANTIC RICHFIELD CO.) 08.01.85 * Columna 6, línea 8 - columna 7, línea 11; columna 8, línea 3 - columna 9, línea 24; ejemplos I y II *	1,2,4-9
Y	US 4192855 A (UOP INC.) 11.03.80 * Todo el documento *	1,2,4-9
A	EP 45170 A (ATLANTIC RICHFIELD CO.) 03.02.82 * Páginas 13-27 *	1,2,5,8

<b>Categoría de los documentos citados</b> X: de particular relevancia Y: de particular relevancia combinado con otro/s de la misma categoría A: refleja el estado de la técnica  O: referido a divulgación no escrita P: publicado entre la fecha de prioridad y la de presentación de la solicitud E: documento anterior, pero publicado después de la fecha de presentación de la solicitud		
<b>El presente informe ha sido realizado</b> <input checked="" type="checkbox"/> para todas las reivindicaciones <input type="checkbox"/> para las reivindicaciones nº:		
<b>Fecha de realización del informe</b> 02.10.96	<b>Examinador</b> M.P. Corral Martínez	<b>Página</b> 1/1

[logo] (19) SPANISH OFFICE OF  
PATENTS AND TRADEMARKS  
  
SPAIN

(11) Publication no.: ES 2 092 429  
(21) Application no.: 9301712  
(51) Int.Cl.<sup>6</sup>: B01D 53/60  
B01D 53/86  
B01J 21/00  
C10G 11/04

(12) PATENT APPLICATION A1

---

(22) Date of application: July 29, 1993

(71) Applicant(s):  
Polytechnic University of Valencia  
Camino de Vera s/n  
46071 Valencia, ES  
Superior Council of Scientific Research

(43) Publication date of application: November 16, 1996

(72) Inventor(s):  
Corma Canós, Avelino  
Palomares Gimeno, Eduardo and  
Rey García, Fernando

(43) Publication date of application pamphlet:  
November 16, 1996

(74) Agent: not stated

---

(54) Title: **Catalyst for elimination of SO<sub>x</sub> and NO<sub>x</sub> from gases, especially from FCC [fluid catalytic cracking] units, and method of preparing it**

(57) Summary:

Catalyst for the elimination of SO<sub>x</sub> and NO<sub>x</sub> from gases, especially FCC units, and method of preparing it.

A description is given of a catalyst formed from oxides of Mg-Al and Cu, and optionally Ce, which is capable of eliminating SO<sub>x</sub> and NO<sub>x</sub> from gaseous wastes. The catalyst acts in an oxidizing atmosphere, with the SO<sub>3</sub> retained on the catalyst being in the form of sulfates. In this step, furthermore, part of the NO<sub>x</sub> decomposes catalytically to N<sub>2</sub> and O<sub>2</sub>. Subsequently, and in the reducing atmosphere, the sulfates break down, generating SH<sub>2</sub>, which is recovered by conventional methods, with the sulfur elimination catalyst being regenerated. Under reducing conditions, this catalyst is also capable of reducing the NO<sub>x</sub> emissions to N<sub>2</sub> and H<sub>2</sub>O.

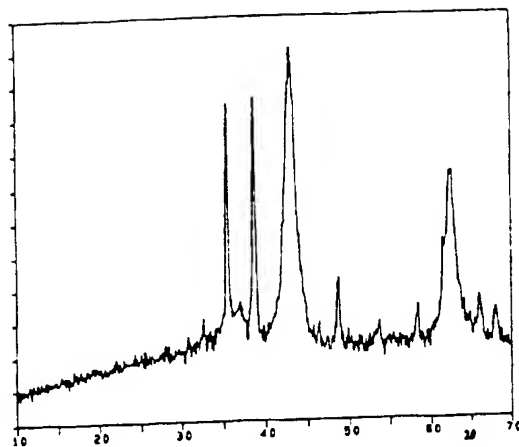


Figure 1

## DESCRIPTION

### Scope of the technique

- Chemical purification of residual gases; elimination of  $\text{SO}_x$  and  $\text{NO}_x$
- Purification of gases during catalytic cracking with molecular sieves
- Mixed oxides of Mg, Al, and Cu.

### Background

Power plants produce on the order of 60% of  $\text{SO}_x$  emissions. On the other hand, refineries produce on the order of 10% of emissions, with FCC (fluid catalytic cracking) units being the chief culprits responsible for these emissions. Environmental coordination agencies in different countries have limited the emissions from these units, requiring procedures that reduce emissions in order to comply with the laws. One procedure consists of desulfurizing the feed stocks scheduled to be cracked in the fluid catalytic cracking units. However, this solution is expensive and is not the most convenient for refineries. Another solution consists of treating the gases with an external catalytic system. This solution, although interesting, brings with it the problems associated with the catalyst particles that are emitted with the gases, as well as the problem of simultaneously and/or easily eliminating the  $\text{SO}_x$  and  $\text{NO}_x$ . Finally, there is a third solution, which consists of adding an additive to the FCC catalyst that is capable of eliminating the  $\text{SO}_x$  and  $\text{NO}_x$  in the regenerator and reactor of the unit. This third solution is

the most economical, and is applied in modern FCC units [I.A. Vasalos et al., *AIChE Annual Meeting*, N.Y., November 15-20, 1987].

### State of the technique

The additives responsible for the elimination of  $\text{SO}_x$  in FCC units are formed from oxides of transition or rare-earth metals, which catalyze the oxidation of  $\text{SO}_2$  to  $\text{SO}_3$  [P.S. Lowell et al., *ICE Proc. Des. Dev.* 10, 384, 1971], among which the  $\text{CeO}_2$  procedure is the one most widely used [A.A. Bhattacharyya et al., *ACS Meeting*, August 30, 1987], supported on  $\text{Al}_2\text{O}_3$  or  $\text{Al}_2\text{O}_3\text{-MgO}$ . The aluminum or aluminum-magnesium oxides react with the  $\text{SO}_3$  in the regenerator of the unit and form the corresponding sulfate. If this sulfate is capable of breaking down in the reactor, the initial oxide is regenerated and the catalytic cycle begins again.

The Mg and La [sic] oxides have a great capacity to form sulfates with  $\text{SO}_3$ , but the sulfates formed are very stable and do not break down easily in the regeneration zone, as a result of which they lose their catalytic activity after the first cycle. On the other hand,  $\text{Al}_2\text{O}_3$  reacts little in the regenerator of the FCC unit with  $\text{SO}_3$ , but the sulfate formed breaks down easily.

With attention to this rationale, mixed oxides of Al and Mg have been designed with which it is hoped to reach a compromise between the adsorption of  $\text{SO}_3$  and decomposition of the sulfate [Yoo et al., *ICE Res.* 27, 1356 (1988); *Applied Catalysis* 13, 169 (1992); US Patent 4,963,520 of 1990; US Patent 4,957,718 of 1990; US Patent 4,957,892 of 1990; US Patent 4,790,982 of 1988; PE Patent 0278535 of 1988; WO Patent 87/06156 of 1987; US Patent 4,529,574 of 1985; US Patent 4,617,175 of 1986].

The catalysts claimed have a relatively high proportion of Al to Al+Mg, given that special emphasis is placed on decomposition of the sulfates formed and therefore on regeneration of the catalysts.

### Brief description of the invention

The present invention incorporates the preparation of catalysts based on Al and Mg oxides with a *high Mg content* and therefore a high  $\text{SO}_3$  adsorption capacity. In this case, and with the purpose of regenerating the catalyst, a *third component* is added which is capable not only of oxidizing the  $\text{SO}_2$  to  $\text{SO}_3$ , but also of catalyzing the decomposition of the sulfate. Thus, using mixed Al and Mg oxides very rich in Mg, adding a suitable catalyst makes it possible to achieve high adsorptions of  $\text{SO}_3$  with high regeneration levels.

The catalysts that are the object of the present invention are thus also highly active in decomposition of the  $\text{NO}_x$  in the oxidizing atmosphere of the regenerator and its reduction in a reducing atmosphere.

### Detailed description of the invention

As a support for the transition-metal oxides and at the same time as agents designed to recover  $\text{SO}_3$  to form sulfates, use is made of mixed Al and Mg oxides that are obtained by coprecipitation of an aqueous solution containing these ions with an alkaline solution.

The solution containing the  $\text{Mg}^{2+}$  and  $\text{Al}^{3+}$  ions is obtained from their soluble salts, e.g.,  $\text{Mg}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$  and  $\text{Al}(\text{NO}_3)_3 \cdot 9 \text{H}_2\text{O}$ . In the corresponding solution, the  $[\text{Mg(II)}]$  and  $[\text{Al(III)}]$  concentrations as well as the  $[\text{Mg(II)}]/[\text{Al(III)}]$  ratio may vary within a broad range, naturally without exceeding the solubility. Considering that the present invention contemplates the use of MgO-rich oxides, it is an indispensable condition that the solution be observed that

$$\frac{[\text{Al(III)}]}{[\text{Al(III)}] + [\text{Mg(II)}]} \leq 0.45$$

For the precipitation process an alkaline solution consisting of a mixture of alkaline hydroxides on carbonates is used, preferably  $\text{NaOH}$  and  $\text{Na}_2\text{CO}_3$ , in sufficient concentration to achieve total precipitation of the Al and Mg from the first solution.

The two solutions are mixed while stirring vigorously. The resulting gels are aged, preferably over a period of between 3 and 20 hours, at a temperature of between 20 and 250°C, and preferably between 60 and 100°C.

After aging, the products are filtered and washed until the filtrate achieves a pH between 6.8 and 7.5. Finally, by calcination at a temperature exceeding 300°C, the product is transformed into a mixed oxide whose  $\text{Al}/(\text{Al}+\text{Mg})$  ratio is equal to or less than 0.45.

The oxidizing agents of  $\text{SO}_2$  and/or the sulfate decomposition catalysts are impregnated on this basis. The present invention uses copper oxide as such an agent, to which cerium oxide may optionally be added.

The copper is incorporated by impregnation on the mixed oxide from a solution of a soluble salt which, on being calcined, produces  $\text{CuO}$  on the mixed oxide. The percentage of  $\text{CuO}$  with respect to the mixture obtained ranges between 1 and 50% by weight and preferably between 2 and 20% by weight. If, in addition to the  $\text{CuO}$ ,  $\text{CeO}_2$  is added to the mixed oxide, this is similarly accomplished by previous or simultaneous impregnation into the  $\text{CuO}$ . The preferred  $\text{CeO}_2$  content is in the range of 2 to 10%.

$\text{CuO}$  can also be incorporated in the catalyst by adding a soluble solution of Cu, e.g.,  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  to the solution containing the Mg and Al salts. In this case, the concentrations are adjusted so that the solution has the Al, Mg, and Cu proportions desired in the final catalyst.

*Catalyst operating system*

The catalyst works in an oxidizing atmosphere, with the  $\text{SO}_3$  retained remaining on the catalyst in the form of sulfates. In this step, in addition, part of the  $\text{NO}_x$  is catalytically decomposed to  $\text{N}_2$  and  $\text{O}_2$ . In a reducing atmosphere, the sulfates subsequently decompose, generating  $\text{SH}_2$ , which is recovered by conventional methods, with the sulfur-elimination catalyst being regenerated. Under reducing conditions, this catalyst is also capable of reducing the  $\text{NO}_x$  emissions to  $\text{N}_2$  and  $\text{H}_2\text{O}$ .

### Examples

#### Example 1:

*Preparation of an Al/Mg/Cu catalyst = 20/70/10*

An aqueous solution (A) (850 ml) of  $\text{Mg}(\text{NO}_3)_2$ ,  $\text{Al}(\text{NO}_3)_3$ , and  $\text{Cu}(\text{NO}_3)_2$  was prepared: 1.05 M in  $\text{Mg}(\text{II})$ , 0.3 M in  $\text{Al}(\text{III})$ , and 0.15 M in  $\text{Cu}(\text{II})$ . While vigorously stirring, this solution was mixed with an aqueous solution (B) consisting of 3.33 M  $\text{NaOH}$  and 1 M  $\text{Na}_2\text{CO}_3$ .

Then the precipitate was left to age for 18 hr at  $80^\circ\text{C}$ , after which it was filtered and washed until the pH of the wash water dropped to 7. The sample obtained was calcined at  $750^\circ\text{C}$ , with a BET area of  $163 \text{ m}^2\cdot\text{g}^{-1}$ . The DRX diagram of the resulting material is presented in Figure 1.

#### Example 2:

*Preparation of an Al/Mg/Cu catalyst = 25/70/5*

Following the same preparation procedure described in Example 1, a catalyst was prepared from a solution (A): 1.05 M in  $\text{Mg}(\text{II})$ , 0.375 M in  $\text{Al}(\text{III})$ , and 0.075 M in  $\text{Cu}(\text{II})$  and an aqueous solution (B): 3.375 M  $\text{NaOH}$  and 1 M  $\text{Na}_2\text{CO}_3$ .

After aging, filtering, washing, and calcining in the manner described in Example 1, a material was obtained with a surface area of  $178 \text{ m}^2\cdot\text{g}^{-1}$ , whose DRX diagram is presented in Figure 2.

#### Example 3:

*Preparation of an Al/Mg/Cu catalyst = 20/70/10 with Ce.*

The procedure begins with a catalyst identical to that obtained in Example 1; after calcining, by pore volume impregnation, the quantity of cerium necessary to obtain 55 wt%  $\text{CeO}_2$  was deposited on the catalyst. After impregnation, the product was dried and calcined at  $750^\circ\text{C}$ , obtaining a material with an area of  $117 \text{ m}^2\cdot\text{g}^{-1}$ , whose DRX diagram is presented in Figure 3.

#### Example 4:

*Preparation of an Al/Mg/Cu catalyst = 10/80/10, with Ce.*

Following the procedure described in Example 1, a catalyst was prepared using a solution (A): 1.2 M in Mg(II), 0.15 M in Al(III), and 0.15 M in Cu(II), and the product was precipitated with an aqueous solution (B): 3.15 M NaOH and 1 M Na<sub>2</sub>CO<sub>3</sub>. As in Example 3, 5% CeO<sub>2</sub> was deposited on the calcined product.

#### **Example 5:**

*Preparation of an Al/Mg/Cu catalyst = 10/70/20 with Ce.*

Following the procedure described in Example 1, a catalyst was prepared using a solution (A): 1.05 M in Mg(II), 0.15 M in Al(III), and 0.3 M in Cu(II), and the product was precipitated with an aqueous solution (B): 3.13 M NaOH and 1 M Na<sub>2</sub>CO<sub>3</sub>. As in Example 3, 5% CeO<sub>2</sub> was deposited on the calcined product.

The final area was 72 m<sup>2</sup>·g<sup>-1</sup>, and the DRX diagram is presented in Figure 4.

#### **Example 6:**

*Use of the catalyst of Example 1 to eliminate SO<sub>x</sub>.*

The SO<sub>x</sub> elimination experiments were conducted in a fixed-bed reactor into which 0.6 g of the catalyst described in Example 1 were placed. After treating at 750°C in a stream of N<sub>2</sub>, the N<sub>2</sub> was cut off and a stream was supplied at 750°C of 1400 ppm SO<sub>2</sub>, 3% O<sub>2</sub>, and the rest up to 100% N<sub>2</sub>. The SO<sub>x</sub> emissions present in the reactor discharge gases were analyzed with a nondispersive I.R. analyzer. The process was stopped when the discharge gases contained 700 ppm of SO<sub>x</sub>. At this time the total quantity of SO<sub>2</sub> adsorbed was 26.1 grams per 100 grams of catalyst.

At this point and in a stream of N<sub>2</sub> the temperature was lowered to 530°C. Once this temperature was reached, a stream of 800 cm<sup>3</sup>·min<sup>-1</sup> of H<sub>2</sub> was sent through for 2 hours.

This cycle was repeated up to four times. In all cases the regeneration achieved was 90% with respect to the previous cycle, with the sulfate-formation capacity after the four cycles being 17 g of SO<sub>2</sub> per 100 grams of catalyst.

If the regeneration is conducted at 620°C, the regeneration is 92% with respect to the first cycle, and the sulfate-formation capacity is 24.6 g of SO<sub>2</sub> per 100 g of catalyst.

#### **Example 7:**

*Use of the catalyst of Example 2 to eliminate SO<sub>x</sub>.*

The catalyst of Example 2, which contained half the copper compared to Example 1, was tested under the same conditions as applied to Example 6. Under these conditions the SO<sub>2</sub> adsorption capacity

is established after two regeneration cycles at 530°C as 17 g of SO<sub>2</sub> per 100 g of catalyst. If the regeneration is conducted at 620°C, 22.4 g of SO<sub>2</sub> per 100 g of catalyst is stabilized.

**Example 8:**

*Use of the catalyst from Example 3 to eliminate SO<sub>x</sub>*

The catalytic activity of the catalyst described in Example 3 was studied under the same conditions as those described for Examples 6 and 7. In this case, the initial adsorption capacity was 20.8 g of SO<sub>2</sub> per 100 g of catalyst, with 18.0 g of SO<sub>2</sub> per 100 g of catalyst being stabilized after two cycles (regeneration temperature of 530°C).

**Example 9:**

*Use of the catalyst of Example 4 to eliminate SO<sub>x</sub>*

In this example the catalytic behavior of the catalyst described in Example 4 is described under the same reaction conditions as in the previous examples. The initial adsorption was 21.4 g of SO<sub>2</sub> per 100 g of catalyst, with a reduction after two regeneration cycles at 530°C to 10.5 g of SO<sub>2</sub> per 100 g of catalyst.

**Example 10:**

*Use of the catalyst of Example 5 to eliminate SO<sub>x</sub>*

In this example, under the reaction conditions of Example 9, the catalytic behavior of the catalyst prepared in Example 5 is described. The initial adsorption was 16.0 g and, after three regeneration cycles, switched to 17.7 g of SO<sub>2</sub> per 100 g of catalyst.

**Example 11:**

*Use of the catalyst of Example 1 in the presence of a commercial FCC catalyst to eliminate SO<sub>x</sub>*

In this example a description is given of the behavior of the catalyst (0.6 g) described in Example 1 for the elimination of SO<sub>2</sub> when proceeding in the presence of a commercial FCC catalyst (14.4 g) based on a rare-earth-free USY zeolite, and after having been treated at 750°C for 8 hours in the presence of 100% H<sub>2</sub>O vapor.

Testing under the conditions of Example 9 gives a quantity of SO<sub>2</sub> adsorbed per 100 g of catalyst of 30.4 g, and after successive cycles the quantity is stabilized at 22.0 g of SO<sub>2</sub> per 100 g of catalyst.



**Example 12:**

*Use of the catalyst of Example 2 in the presence of a commercial FCC catalyst to eliminate  $SO_x$*

The catalyst of Example 2 was tested under the same conditions as described in Example 11, with the initial quantity of  $SO_2$  adsorbed being 37.0 g and with stabilization at 20.0 g of  $SO_2$  per 100 g of catalyst.

**Example 13:**

*Use of the catalyst of Example 1 in the presence of a commercial FCC catalyst to eliminate  $NO_x$*

In this example the activity of the catalyst in the decomposition of  $NO_x$  is described.

[Testing of] the catalyst of Example 1: After mixing and treating with FCC catalyst as in Example 11, 0.6 g of catalyst and 14.4 g of FCC catalyst were placed in the reactor. After treating with  $H_2$  at  $530^\circ C$  and passing through  $N_2$ , the temperature was increased to  $750^\circ C$ . Then a stream of 400 ppm of NO in  $N_2$  was sent through, with a volume of flow of  $1600\text{ cm}^3\cdot\text{min}^{-1}$ . The decomposed  $NO_x$  was calculated, analyzing the residual  $NO_x$  by chemi-luminescence. The process was stopped when the NO content in the discharge gases was 200 ppm. Under these conditions, 2.33 g of NO were broken down per 100 g of catalyst.

**Example 14:**

*Influence of the NO decomposition temperature*

In this example the influence of the NO decomposition temperature is described.

The same catalyst as in Example 13 was studied for the decomposition of NO at different reaction temperatures, and the results are given in the following table:

Temperature ( $^\circ C$ )	Decomposition ( $\text{cm}^3$ )
500	4.0
600	7.4
700	11.3
750	10.4
800	7.05

**Description of figures:**

- Figure 1 X-ray diffraction diagram of the catalyst of Example 1 (ratio of Al(Mg/Cu= 20/70/10)).  
Ordinate: intensity (arbitrary units)
- Figure 2 X-ray diffraction diagram of the catalyst of Example 2 (ratio of Al(H<sub>3</sub>/Cu=25/70/5)).  
Ordinate: intensity (arbitrary units)
- Figure 3 X-ray diffraction diagram of the catalyst of Example 3 (ratio of Al(Mg/Cu=20/70/10 –  
CeO<sub>2</sub> 5%)).  
Ordinate: intensity (arbitrary units)
- Figure 4 X-ray diffraction diagram of the catalyst of Example 5 (ratio of Al(Mg/Cu=10/80/10 –  
CeO<sub>2</sub> 5%)).  
Ordinate: intensity (arbitrary units)

## CLAIMS

1. A catalyst capable of reducing the  $\text{SO}_x$  and  $\text{NO}_x$  emissions formed from a component capable of oxidizing  $\text{SO}_2$  to  $\text{SO}_3$ , of breaking down and/or reducing the  $\text{NO}_x$ , and of catalyzing the decomposition of the sulfate formed on another component, characterized by the fact that the first component is made up of  $\text{CuO}$  or  $\text{CuO} + \text{CeO}_2$  and the second of a mixed oxide of  $\text{Al} + \text{Mg}$ , in which the  $\text{Al}$  to  $\text{Al} + \text{Mg}$  proportion is equal to or less than 0.45 and in which the copper oxide content ranges between 1 and 50 wt%, preferably between 2 and 20%, of the catalyst, and the content of cerium oxide,  $\text{CeO}_2$ , may reach as high as 10 wt%.
2. Preparation of the catalyst according to Claim 1, characterized by the fact that the component of mixed  $\text{Al}$  and  $\text{Mg}$  oxides is prepared by precipitating an aqueous solution of soluble aluminum and magnesium salts with an alkaline solution, wherein the molar proportion of  $\text{Al(III)}$  to the sum of  $\text{Al(III)}$  plus  $\text{Mg(II)}$  in the solution is less than 0.45.
3. Preparation of the catalyst according to Claim 1, characterized by the fact that the precipitating solution contains  $\text{NaOH}$  and  $\text{Na}_2\text{CO}_3$ , preferably in a molar proportion of  $\text{NaOH}$  to  $\text{Na}_2\text{CO}_3$  of 3.
4. Preparation of the catalyst according to Claims 1 to 3, characterized by the fact that the  $\text{Cu}$  can be introduced by adding a soluble salt of copper (II) to the solution described in Claim 2.
5. Preparation of the catalyst according to Claims 1 to 4, characterized by the fact that the precipitate is left to age between 0 and 30 hours, and preferably between 3 and 20 hours, at a temperature of between  $20^\circ\text{C}$  and  $250^\circ\text{C}$ , and preferably between 20 and  $100^\circ\text{C}$ .
6. Preparation of the catalyst according to Claims 1 to 5, characterized by the fact that the aged precipitate is filtered and washed until the pH of the wash water is less than 7.5, and is calcined at a temperature exceeding  $300^\circ\text{C}$ .
7. Preparation of the catalyst according to Claims 1 to 6, characterized by the fact that by impregnation of the mixed oxide of  $\text{Al}$  and  $\text{Mg}$ ,  $\text{CuO}$  can be deposited on the resulting material after calcination according to Claim 6.
8. Preparation of the catalyst according to Claims 1 to 7, characterized by the fact that by impregnation of the mixed oxide of  $\text{Al}$  and  $\text{Mg}$ ,  $\text{CeO}_2$  can be deposited on the resulting material after calcination according to Claim 6.
9. A catalyst according to Claims 1 to 8, characterized by the fact that it is capable of reducing the  $\text{SO}_x$  and  $\text{NO}_x$  emissions at stationary sources by means of a process that entails one step in an oxidizing atmosphere and another step in a reducing atmosphere.